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(54) **Fluoroelastomers based on vinylidene fluoride, hexafluoropropene and tetrafluoroethylene.**

(57) The invention relates to new fluoroelastomers endowed with both a low T<sub>g</sub> and a low compression set at low temperature, characterized by the following monomeric composition:

vinylidene fluoride:	60.5 to 64% by weight
hexafluoropropene:	30 to 33% by weight
tetrafluoroethylene:	5 to 8% by weight.

**EP 0 445 839 A1**

The present invention relates to new fluoroelastomers, i.e., terpolymers of vinylidene fluoride, hexafluoropropene and tetrafluoroethylene.

US-A-4,123,603 discloses elastomeric terpolymers having the following monomeric composition:

- vinylidene fluoride: 57 to 61% by weight
- 5 hexafluoropropene: 27 to 31% by weight
- tetrafluoroethylene: 10 to 14% by weight.

These terpolymers are endowed with a low glass transition temperature ( $T_g$ ) and a low compression set at low temperature.

- The preferred product according to the above patent has the following monomeric composition by weight: 59% of vinylidene fluoride, 29% of hexafluoropropene and 12% of tetrafluoroethylene. The average  $T_g$  of four samples of this product is 24.75 °C. The compression set of the above samples, after a 70-hour compression test at 0 °C (according to ASTM-D 395, method B) is lower than or equal to 20%, when measured at room temperature within one hour after completion of the test.

- The above patent states and proves by means of several comparison examples that within the compositional range disclosed therein it is not possible to obtain, at the same time, a low  $T_g$  and a low compression set at low temperature.

It has now surprisingly been found that there is another compositional range of terpolymers with which said two properties can be obtained simultaneously.

- Thus, it is an object of the present invention to provide new fluoroelastomers based on vinylidene fluoride, hexafluoropropene and tetrafluoroethylene which are simultaneously endowed with both a low  $T_g$  and a low compression set at low temperature.

Another object is to provide fluoroelastomers of the above type which exhibit also a very low crystallinity, lower than that of the above known product, and low TR (temperature retraction) values.

- A further object is to provide fluoroelastomers of the above type which furthermore exhibit a higher vulcanization rate than that of the above known product.

These and still other objects are achieved by the fluoroelastomers according to the present invention which are characterized by the following monomeric composition:

- vinylidene fluoride: 60.5 to 64% by weight
- hexafluoropropene: 30 to 33% by weight
- 30 tetrafluoroethylene: 5 to 8% by weight.

These fluoroelastomers are endowed with a glass transition temperature ( $T_g$ ) which is lower than or equal to about -25 °C and show a compression set, after a 70-hour compression test at 0 °C on a disc (according to ASTM D 395, method B), lower than or equal to about 18%, when measured at 23 °C after 30 minutes.

- Furthermore, they are endowed with a low crystallinity and low TR values. In addition they exhibit, as compared to the above known terpolymer, a higher vulcanization rate, which results in a higher productivity of the corresponding apparatus for the production of shaped articles.

They are particularly suitable for those applications in which a low  $T_g$  and a low compression set at low temperature are required, in particular for the manufacture of O-rings and shaft seals.

- In these applications a lowering of the  $T_g$  and, even more important, of the TR values without adversely affecting the compression set values is a need particularly felt by the users, for which a gain of a few degrees centigrade represents substantial technological progress.

- The terpolymers according to the present invention may be prepared by means of known methods such as, for example, those described in Kirk Othmer, Encyclopaedia of Chemical Technology, vol. 8, pages 500 ff., 1979. Examples of suitable polymerization methods are, in particular, bulk polymerization, polymerization in a solution of organic solvents and polymerization in a water emulsion or suspension. Examples of suitable radical polymerization initiators are inorganic peroxides such as ammonium or potassium persulphates, redox systems such as persulphate-bisulphite and organic peroxides such as, for example, benzoyl peroxide and dicumyl peroxide.

- As chain transfer agents it is possible to use, for example, ethyl acetate and/or diethyl malonate.

Preferably it is operated in an aqueous emulsion, at temperatures ranging from about 25 to about 150 °C and under a pressure ranging from about 8 to about 80 atmospheres.

Another object of the present invention is represented by the articles manufactured from the terpolymers according to the present invention.

- The following examples are given for merely illustrative purposes and are not to be construed as being a limitation of the scope of the present invention.

Examples 1 and 2 are within the compositional range of the present invention, while example 3 relates to the preferred composition of the above US-A-4,123,603.

The preparation of the polymers by means of the emulsion polymerization process was carried out in a manner such as to achieve, for all elastomers of the present examples 1 to 3, the same average molecular weight (deduced from the Mooney viscosity ML (1 + 10) at 121 °C and the intrinsic viscosity) and the same molecular weight distribution.

Therefore, the chemico-physical properties indicated in Table 1 depend exclusively on the monomeric composition of the polymers.

### EXAMPLE 1

Employed was a 10-liter reactor equipped with stirrer. After vacuum had been applied 6,500 g of water were fed and pressure was generated in the reactor by means of a monomeric mixture having the following molar composition:

vinylidene fluoride: 58%  
hexafluoropropene: 38%  
tetrafluoroethylene: 4%

The reactor was heated up to 85 °C, reaching a pressure of 19 bar. Then there were added 260 ml of ethyl acetate as an aqueous solution at 66 ml/l and 13 g of ammonium persulphate as an aqueous solution at 150 g/l.

During polymerization, the pressure was maintained constant by feeding the monomers in the following molar ratio:

vinylidene fluoride: 78.5%  
hexafluoropropene: 16.5%  
tetrafluoroethylene: 5%

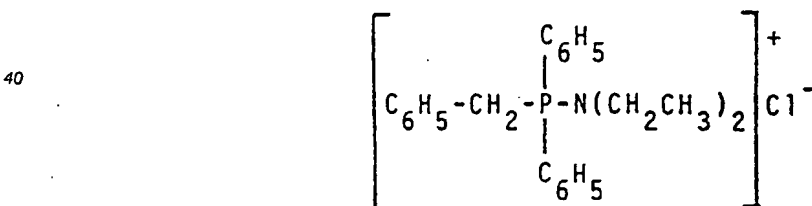
After obtainment of 2,800 g of polymer with a polymerization time of 55 minutes, the whole system was cooled to room temperature. The emulsion was discharged and then coagulated by addition of an aqueous aluminium sulphate solution. The polymer was separated, washed with water and dried in an air-circulation oven at 60 °C until its water content was below 0.2% by weight.

According to <sup>19</sup>F-NMR analysis, the polymer exhibited the following monomeric composition:

vinylidene fluoride: 63% by weight  
hexafluoropropene: 30.6% by weight  
tetrafluoroethylene: 6.4% by weight

The polymer was subjected to several determinations and tests, which are reported in Table 1.

A vulcanization blend was prepared by using a master batch M1 containing 50% of bisphenol AF and 50% of the fluoroelastomer and a master batch M2 containing 30% of an accelerator and 70% of the fluoroelastomer. The accelerator had the formula:



The blend contained:

terpolymer 100 parts by weight  
M1 4 parts by weight  
M2 1.5 parts by weight  
Ca(OH)<sub>2</sub> 6 parts by weight  
MgO 3 parts by weight  
MT black 25 parts by weight

### EXAMPLE 2

The procedure of example 1 was followed, except that the reactor was pressurized with the following monomeric mixture:

vinylidene fluoride: 59% by mols  
hexafluoropropene: 36% by mols  
tetrafluoroethylene: 5% by mols

During polymerization, the pressure was maintained constant by feeding the monomers in the following molar ratio:

vinylidene fluoride: 77.2%  
hexafluoropropene: 16.5%  
tetrafluoroethylene: 6.3%

There were obtained 2,800 g of a terpolymer which, according to  $^{19}\text{F}$ -NMR analysis, exhibited the following monomeric weight composition:

vinylidene fluoride: 61.4%  
hexafluoropropene: 30.8%  
tetrafluoroethylene: 7.8%

The terpolymer was subjected to the same determinations and tests as that of example 1. The results are reported in Table 1.

### EXAMPLE 3

For comparison purposes, the preferred terpolymer of US-A-4,123,603 was prepared. The modalities were identical with those of example 1, with the exception that:

(a) the reactor was pressurized with a monomer mixture of the following molar composition:

vinylidene fluoride: 56%  
hexafluoropropene: 36%  
tetrafluoroethylene: 8%

(b) during polymerization, the pressure was maintained constant by feeding the monomers in the following molar ratio:

vinylidene fluoride: 74.7%  
hexafluoropropene: 15.6%  
tetrafluoroethylene: 9.7%

There were obtained 2,800 g of terpolymer which, according to  $^{19}\text{F}$ -NMR analysis, exhibited the following monomeric weight composition:

vinylidene fluoride: 59.5%  
hexafluoropropene: 28.6%  
tetrafluoroethylene: 11.9%

The results obtained with the above terpolymers and the products made therefrom are summarized in the following Table 1.

TABLE 1

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A - DETERMINATIONS ON THE ELASTOMER:			
Nature of the test	Ex. 1	Ex. 2	Ex. 3
Tg midpoint (ASTM D 3418-82)	-26°C	-25,2°C	-25,4°C
Tf1 (ASTM D 3418-82)	51,3°C	42,7°C	44,9°C
Tf2	72°C	58°C	63,7°C
DH1	0,03	0,11	0,10
DH2	0,08	0,02	0,12
DH1 + DH2	0,11	0,13	0,22
DMS (METHOD ISO R. 5378)			
T $\alpha$	-19°C	-19°C	-18°C
G'(10°C)	1.2 N/mm	1.1 N/mm	1.35 N/mm
Intrinsic viscosity (ASTM D 1416-83)	59 ml/g	60 ml/g	58 ml/g
Mw/Mn (ASTM D 3593-80)	2,6	2,5	2,4
Mooney viscosity			
ML(1+10') at 121°C (Mooney unit)			
(ASTM D 1646-82)	19	20	20

TABLE 1 (continued)

5	B - TESTS ON THE VULCANIZATION MIX:			
	Nature of the test	Ex. 1	Ex. 2	Ex. 3
10	Mooney viscosity of the mix (ASTM D 1646-82)			
15	ML(1+10') at 121°C (Mooney unit)	36	37	37
	Mooney scorch at 135°C			
20	(ASTM D 1646-82)			
	MV(pounds x inch)	12	14	14
25	t $\Delta$ 15	46'30"	47'30"	45'45"
	ODR 177°C, ARC $\pm$ 3°			
30	(ASTM D 2084-81)			
	ML (pounds x inch)	3.4	3.5	3.5
	MH (pounds x inch)	96.5	100	99.5
35	ts2 (sec)	171	170	177
	t'90 (sec)	243	235	267
40	V <sub>max</sub> (pounds x inch/sec)	3	3.2	2.7

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TABLE 1 (continued)

5	C - TESTS ON VULCANIZED SPECIMENS:			
	Nature of the test	Ex. 1	Ex. 2	Ex. 3
10	AFTER VULCANIZATION IN PRESS			
	at 170°C for 10' (ASTM D 412-83)			
15	100% modulus (MPa)	3.7	3.6	3.5
	Tensile strength (MPa)	10.6	10.0	10.5
	Elongation at break (%)	245	250	256
20	IRHD (points) (ASTM D 2240-81)	68	68	68
	AFTER POST-TREATMENT at 250°C			
25	for 24 hours, including 8 h			
	rise			
30	(ASTM D 412-83)			
	100% modulus (MPa)	5.4	5.5	5.3
35	Tensile strength (MPa)	14.5	14.5	14.4
	Elongation at break (%)	188	200	194
	IRHD (points) (ASTM D 2240-81)	69	70	70
40	TR TEST (ASTM D 1329)			
	TR 10%	-18.4°C	-19°C	-18°C
45	TR 30%	-14.1°C	-14.5°C	-14.1°C
	TR 50%	-10.7°C	-11.5°C	-10.6°C

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TABLE 1 (continued)

5	COMPRESSION SET (ASTM D 395			
	method B)			
10	70 h at 0°C, disc (12.5 x 29 mm)			
	- reading at 0°C after 30 sec.	73%	73%	76%
15	- reading at 23°C after 30 min.	18%	17%	20%
	- reading at 23°C after 28 h	10%	9%	11%
20	70 h at 23°C: O-ring D 214			
	(ASTM 395/B)			
25	- reading at 23°C after 30 min.	20%	20%	22%

From a comparison of results obtained with the terpolymers according to the present invention (examples 1 and 2) and with that of the art (example 3) the following can be derived:

1. the T<sub>g</sub> and TR values of the products according to the present invention are as low as, and often lower than those of the known product;
2. the data relating to DH1 + DH2 and DMS show that the products according to the present invention exhibit a lower crystallinity;
3. the compression set after compression tests at 0°C and 23°C is lower for the products of the present invention;
4. in spite of a lower tendency to scorch (see the Mooney Scorch data at 135°C; t<sub>Δ15</sub>), the vulcanization rate of the terpolymers according to the present invention is higher (see ODR data at 177°C: V<sub>max</sub>).

#### 40 EXAMPLES 4 to 6

It was operated as in example 1, except that the reactor was pressurized with the following monomeric mixtures:

45		Ex. 4	Ex. 5	Ex. 6
	vinylidene fluoride	58.5% by mols	57 % by mols	57.5% by mols
	hexafluoropropene	36.5% by mols	38.5% by mols	39 % by mols
50	tetrafluoroethylene	5 % by mols	4.5% by mols	5.5% by mols

and except that, during the polymerization, the pressure was maintained constant by feeding the monomers in the following molar ratios:

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	Ex. 4	Ex. 5	Ex. 6
vinylidene fluoride	76.7% by mols	77.8% by mols	78.2% by mols
5 hexafluoropropene	17.5% by mols	17.0% by mols	17.2% by mols
tetrafluoroethylene	5.8% by mols	5.2% by mols	4.6% by mols

In each instance there were obtained 2800 g of terpolymer which, according to  $^{19}\text{F}$ -NMR analysis,  
 10 exhibited the following weight composition:

	Ex. 4	Ex. 5	Ex. 6
15 vinylidene fluoride	61% by mols	62 % by mols	62.5% by mols
hexafluoropropene	32% by mols	31.5% by mols	32 % by mols
tetrafluoroethylene	7% by mols	6.5% by mols	5.5% by mols

20 The terpolymers were subjected to the same determinations and tests as those of examples 1 to 3.  
 The results are reported in Table 2.

TABLE 2

5	<b>A - DETERMINATIONS ON THE ELASTOMER:</b>			
	Nature of the test	Ex. 4	Ex. 5	Ex. 6
10	Tg midpoint (ASTM D 3418-82)	-25.4 °C	-26 °C	-26.2 °C
	Tf1 (ASTM D 3418-82)	44 °C	48.2 °C	50.1 °C
15	Tf2	72 °C	58 °C	63.7 °C
	DH1	0.05	0.03	0.08
20	DH2	0.05	0.09	0.10
	DH1 + DH2	0.10	0.12	0.18
25	DMS (METHOD ISO R537B)			
	T $\alpha$	-19 °C	-19 °C	-19 °C
30				
	G'(10°C)	<1 N/mm	1.0 N/mm	1.2 N/mm
35	Intrinsic viscosity	59 ml/g	60 ml/g	60 ml/g
	(ASTM D 1416-83)			
40	Mw/Mn (norma ASTM D 3593-80)	2.4	2.6	2.5
	Mooney viscosity			
45	ML(1+10') at 121°C (Mooney unit)			
	(ASTM D 1646-82)	21	20	20

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TABLE 2 (continued)

5	<b>B - TESTS ON THE VULCANIZATION MIX:</b>			
10	Nature of the test	Ex. 4	Ex. 5	Ex. 6
	MOONEY VISCOSITY OF THE MIX			
	(ASTM D 1646-82)			
15	ML(1+10') at 121°C (Mooney unit)	38	37	37
	MOONEY SCORCH AT 135°C			
20	(ASTM D 1646-82)			
	MV (pounds x inch)	15	14	14
25	t $\Delta$ 15	48'00"	46'45"	47'50"
	ODR 177°C, ARC $\pm$ 3°			
30	(ASTM D 2084-81)			
	ML (pounds x inch)	3.7	3.5	3.5
35	MH (pounds x inch)	105	100	99.8
	ts2 (sec)	173	170	172
40	t'90 (sec)	230	236	240
	V <sub>max</sub> (pounds x inch/sec)	2.9	3.1	3.2

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TABLE 2 (continued)

5	<b>C - TESTS ON VULCANIZED SPECIMENS:</b>			
	<b>Nature of the test:</b>	<b>Ex. 4</b>	<b>Ex. 5</b>	<b>Ex. 6</b>
10	After vulcanization in press			
	At 170°C FOR 10' (ASTM D 412-83)			
15	100% Modulus (MPa)	3.8	3.7	3.7
	Tensile strength (MPa)	11	10.5	10.3
	Elongation at break (%)	280	250	248
20	IRHD (points) (ASTM D 2240-81)	68	68	68
	After post-treatment At 250°C for			
25	24 hours including 8 h rise			
30	(ASTM D 412-83)			
	100% Modulus (MPa)	5.6	5.5	5.3
35	Tensile strength (MPa)	14.7	14.5	14.5
	Elongation at break (%)	190	188	200
40	IRHD (points) (ASTM D 2240-81)	70	70	70
	TEST TR (ASTM D 1329)			
45	TR 10%	-19.3 °C	-19.4 °C	-19.1 °C
	TR 30%	-14.8 °C	-15.4 °C	-15.1 °C
50	TR 50%	-12.1 °C	-12.9 °C	-12.8 °C

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TABLE 2 (continued)

	Ex. 4	Ex. 5	Ex. 6
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**Claims**

1. Fluoroelastomers having a low T<sub>g</sub> and a low compression set at low temperature, characterized by the following monomeric composition:
  - vinylidene fluoride: 60.5 to 64% by weight
  - hexafluoropropene: 30 to 33% by weight
  - tetrafluoroethylene: 5 to 8% by weight.
2. Articles manufactured from a fluoroelastomer according to claim 1.



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## EUROPEAN SEARCH REPORT

Application Number

EP 91 10 3612

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US-A-2 968 649 (J. PAILTHORP ET AL.) * claims; example 1 * - - -	1-2	C 08 F 214/22 // (C 08 F 214/22 C 08 F C 08 F 214:26 C 08 F 214:28 )
A,D	FR-A-2 393 012 (DU PONT) * claims; examples * - - - - -	1-2	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 08 F
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of search 19 June 91	Examiner HOFFMANN K.W.
<div><div><b>CATEGORY OF CITED DOCUMENTS</b> X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention</div><div>E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons ----- &amp;: member of the same patent family, corresponding document</div></div>			